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(54) **Hydrogenation of Polymers**

(57) A process for the hydrogenation of polymers and copolymers and for the selective hydrogenation of block copolymers comprises contacting said polymer in solution with gaseous or dissolved hydrogen in the presence of a heterogeneous solid particulate catalyst comprising a solid porous

particulate support made from a material selected from the group consisting of carbon, alumina, silica and keiselguhr having deposited upon it one or more catalytic metals selected from the group consisting of Ru, Rh, Pd, Ir, Pt, Mn, Cr, Fe, Co, Ni, U, Cu, Nd, In, Sn, Zn, Ag, Cr and alloys containing one or more of the said metals.

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SPECIFICATION

Production of Stable Polymers

This invention relates to stabilized polymers; more particularly it relates to processes whereby the stability of polymeric materials may be increased.

5 The structural and engineering uses of polymeric materials continues to grow rapidly in areas as diverse as protective paint coverings, wire insulations, structural panels for automobiles and piping of all kinds. In such uses the stability of the polymer is of paramount importance. The polymer must be able to retain its mechanical and physical properties over extended periods of time in what for the normal polymer is a hostile environment. Organic polymers are highly susceptible to oxidative
10 degradation which can be considerably aggravated by exposure to the UV radiation in sunlight. This susceptibility arises from the structural unsaturation of many polymers which contain reactive carbon-carbon double bonds and the fact that the aromatic ring absorbs the UV light readily.

As a consequence of this phenomenon such structural applications are at present satisfied predominantly by polymers without unsaturation. These are frequently based on vinyl chloride acrylic
15 monomers. Blends of homopolymers and A-B-A type block copolymers have been used in preventing stress-cracking in polyolefins and to improve the impact resistance of polyolefins and olefin copolymers.

It is therefore an object of the present invention to improve the chemical stability and mechanical strength of polymers, copolymers and block co-polymers, particularly those which are subject to ultra
20 violet radiation. It is a further object of the present invention to remove the carbon-carbon double bond unsaturation which produces the described instability in polymers, copolymers and block co-polymers and thus enable a much wider range of these polymers to be used for external and other hostile environments.

One way in which the unsaturation may be removed is by hydrogenation. However, the ability to
25 hydrogenate any substrate using a heterogenous catalyst in the liquid phase is highly dependent on the ability of the substrate to diffuse to and away from the catalyst surface. Such diffusion is much restricted as the molecular size or molecular weight of the substrate increases. As the molecular size increases it is also easy to envisage severe steric restrictions which would prevent the reactive point of the molecule from reaching the catalytic site. In the case of a heterogeneous liquid phase catalyst
30 comprising a catalytic metal deposited upon a particulate solid support, the use of high molecular weight polymeric substrates might be expected to provide a stringent test of availability of the catalytic metal. Furthermore, it is necessary that there be selective hydrogenation of a block copolymer. In a styrene-butadiene-styrene three block co-polymer selective hydrogenation of the butadiene block is desirable since the block loses its pliability or rubbery character if the styrene section is also completely
35 hydrogenated. Such loss is undesirable and seriously undermines the usefulness of the polymer.

According to one aspect of the present invention a process for the hydrogenation of polymers and copolymers and for the selective hydrogenation of block copolymers comprises contacting said polymer in solution with gaseous or dissolved hydrogen in the presence of a heterogeneous solid
40 particulate catalyst comprising a solid porous particulate support made from a material selected from the group consisting of carbon, alumina, silica and kieselguhr having deposited upon it one or more catalytic metals selected from the group consisting of Ru, Rh, Pd, Ir, Pt, Mn, Cr, Fe, Co, Ni, U, Cu, Nd, In, Sn, Zn, Ag, Cr and alloys containing one or more of the said metals.

Preferably the process is one of selective hydrogenation of olefinic unsaturation rather than that of the aromatic ring.

45 Polymers with which the invention may be used are polystyrene, polyacrylics, acrylic co-polymers, vinyl co-polymers, cyclic and acyclic diene co-polymers, e.g. co-polymers of butadiene.

The invention also includes polymers when stabilized in accordance with the foregoing process.

We have found that the invention gives greater selectivity in reducing polymeric unsaturation under less forcing conditions than with prior art catalyst such as nickel or cobalt.

50 Preferably the polymeric compound is suspended in a rapidly stirred non-polar solvent in an autoclave at a temperature within the range 50°—200°C and having an atmosphere of hydrogen at a pressure within the range 1 to 50 atmospheres. A suitable non-polar solvent is cyclohexane. Other non-polar solvents which may be used are chlorinated hydrocarbons. Polar solvents such as aliphatic alcohols, e.g. ethanol may also be used when appropriate.

55 A catalyst which we prefer to use is palladium deposited upon a solid porous particulate support such as carbon. Other supports which may be used are alumina, kieselguhr and porous silica gel. One method of preparing a palladium on carbon catalyst in which the palladium is deposited only upon the external surfaces of a porous carbon support is described in British Patent Application No. 21 100/76 dated 21 st May 1976. Such a catalyst is eminently suitable for the
60 selective hydrogenation of high molecular weight polymers in the present invention. In the specification, the novel catalyst which is described therein comprises metallic palladium deposited onto a porous particulate solid such as charcoal in such a way that the metallic palladium remains on the outside of the particle and is deposited only within the pore mouths of those pores having a diameter than 50Å units.

Another catalyst suitable for use in the present invention is that described in our co-pending British application 8932/76, United States application No. 774042 and published on 8th September 1977 in German Offenlegungsschrift 2 709 525. This specification describes the use of this catalyst for the purification of terephthalic acid.

As described in these applications it is frequently preferably to use a mixture or alloy as the catalytic metal e.g. an alloy of two platinum group metals or one or more platinum group metals and a base metal.

Catalysts embodying both of the above described features may be used in the present invention. For example an alloy of palladium with another platinum group metal or a base metal may be deposited on the external surface of porous carbon particles or granules and only within the pore mouths of those pores having a diameter greater than 50 Å units.

Example 1

Hydrogenations were conducted in a 1 litre dashed autoclave under an initial hydrogen pressure of 4 atmospheres. The polymer used was a styrene-butadiene-styrene ABA three block copolymer having 50% of the total polymer as polystyrene and a molecular weight of approximately 200,000. The polymer (obtained from Aldrich Chemical Co.) was dissolved in cyclohexane (Analer Grade) to give a 1% by weight solution. The autoclave was normally charged with 500 ml of polymer solution.

Products were analysed and conversions estimated by following the disappearance of the strong infra-red absorption bands at 970 cm⁻¹ and 700 cm⁻¹ for the olefin and styrene respectively. These infra-red spectra were obtained from polymer films cast directly on NaCl plates by allowing the solvent to evaporate.

Since this procedure gave polymer films of varying thicknesses an absorbance ratio or relative absorbance was calculated using the strongest hydrocarbon band at 2920 cm⁻¹ as an internal reference. Conversions were estimated by relating this relative absorbance to that obtained using the polymer feed. While it is recognized that this procedure is subject to systematic errors the simplicity of this method is felt to justify its use. It is believed that this method does give a fair representation of relative catalytic activity and selectivity. Results are given in Table 1.

Table 1

Run No.	Feed	Catalyst	Type	Weight g	Max temp	Time at T	Conversion		
					°C	Max Mins	BD %	Styrene %	
5	A	10% Pd/C	(a)	0.4	150	60	4	6	
15	A	10% Pd/C	(b)	1.0	150	60	54	62	
2	A	3% Pd/C	(b)	0.4	150	60	12	4	
9	A	1% Pt/Al ₂ O ₃	(c)	1.9	150	60	98	82	
12	A	1% Pt/Al ₂ O ₃	(c)	1.9	105	15	96	82	
14	A	1% Pt/Al ₂ O ₃	(c)	1.9	80	60	88	74	
16	B	1% Pt/Al ₂ O ₃	(c)	1.0	145	120	35	—	
17	C	1% Pt/Al ₂ O ₃	(c)	1.0	110	30	—	2	
18	C	1% Pt/Al ₂ O ₃	(c)	1.0	150	60	—	4	

feed: A Styrene/Butadiene ABA block copolymer
B Linear air and trans polybutadiene
C Polystyrene

Catalyst type (a) Standard deposition of Pd on charcoal

(b) Deposition according to BP Appn. 21100/76

(c) Standard deposition of Pt on alumina using chloroplatinic acid impregnation of alumina powder

Comparison of run 5 with runs 15 and 2 demonstrates a considerable improvement in hydrogenation activity by virtue of deposition of the catalytic metal on the external surfaces of the particulate support.

Runs 9, 12 and 14 indicate the possibility of favourable selectivity being obtained using Pt on alumina support. Pt/Al₂O₃ is the most active.

Runs 16, 17 and 18 are blanks on individual polymer feeds rather than the block copolymer.

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Example 2**5% Pt on SiO₂***Reaction Conditions:*

5	Substrate:	1% by weight styrene butadiene block copolymer ABA	5
	H ₂ pressure:	P ₁ =150 psig P ₂ =147 psig	
10	Temp °C:	T=120°C	10
	H ₂ flow rate:	50 ml min ⁻¹	
	Feed rate:	4 gh ⁻¹	
	WHSV:	0.8 h ⁻¹	
	H ₂ /Oil:	2.5	
	% Conversion:	% styrene 100 (±) % olefin 100 (±)	

Example 3

15	Catalyst=5 g	5% Pt on SiO ₂	15
	<i>Reaction conditions:</i>		
	Substrate:	1% by weight styrene butadiene block copolymer ABA	
20	H ₂ pressure:	P ₁ =150 psig P ₂ =149 psig	20
	Temp:	T=120°C	
	H ₂ flow rate:	40 ml min ⁻¹	
	Feed rate:	1.58 gh ⁻¹	
	WHSV:	0.316 h ⁻¹	
25	H ₂ /Oil:	=5.1	25
	Conversion:	% styrene: 100 (±) % olefin: 100 (±)	

Example 4

	Catalyst: 5 g.	10.0 by wt. Pd on charcoal deposition according to British Patent Appln. 21 100/76 dated 21st May 1976	
30	<i>Reaction conditions:</i>		30
	Substrate:	1% by weight styrene butadiene ABA block copolymer	
	H ₂ pressure:	P ₁ =150 psig P ₂ =145 psig	
35	Temp	=150°C	35
	H ₂ flow rate:	50 ml min ⁻¹	
	Feed rate:	28 gh ⁻¹	
	WHSV	5.6 h ⁻¹	
	H ₂ /Oil	0.36	
40	Conversion:	% styrene=93% % olefin=91.6%	40

Claims

1. A process for the hydrogenation of polymers and copolymers and for the selective hydrogenation of block copolymers comprising contacting said polymer in solution with gaseous or dissolved hydrogen in the presence of a heterogeneous solid particulate catalyst comprising a solid porous particulate support made from a material selected from the group consisting of carbon, alumina, silica and kieselguhr having deposited upon it one or more catalytic metals selected from the group consisting of Ru, Rh, Pd, Ir, Pt, Mn, Cr, Fe, Co, Ni, U, Cu, Nd, In, Sn, Zn, Ag, Cr and alloys containing one or more of the said metals.
2. A process according to Claim 1 for the selective hydrogenation of an unsaturated olefin.
3. A process according to Claim 1, wherein the polymer is selected from the group consisting of polystyrene, polyacrylics, acrylic co-polymers, vinyl copolymers, cyclic and acyclic diene co-polymers.
4. A process according to Claim 3, wherein the co-polymer is a co-polymer of butadiene.
5. A process according to Claim 1, wherein the polymer is contacted with an agitated non-polar solvent at a temperature falling within the range 50—200°C and at a pressure within the range 1 to 50 atmospheres.
6. A process according to Claim 5, wherein the non-polar solvent is selected from the group consisting of cyclohexane, chlorinated hydrocarbons and aliphatic alcohols.
7. A process according to any preceding claim, wherein the catalyst comprises palladium deposited upon a solid, porous and particulate carbon support.
8. A process according to Claim 1, wherein the catalyst comprises platinum deposited on solid, porous and particulate alumina or silica.